

# Anisotropic superexchange of a $90^\circ$ Cu-O-Cu bond

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The magnetic anisotropy of a rectangular Cu-O-Cu bond is investigated in second order of the spin-orbit interaction. Such a bond is characteristic for cuprates having edge sharing  $\text{CuO}_2$  chains, and exists also in the  $\text{Cu}_3\text{O}_4$  plane or in ladder compounds. For a ferromagnetic coupling between the copper spins an easy axis is found perpendicular to the copper oxygen plaquettes in agreement with the experimental spin structure of  $\text{Li}_2\text{CuO}_2$ . In addition, a pseudo-dipolar interaction is derived. Its estimation in the case of the  $\text{Cu}_3\text{O}_4$  plane (which is present for instance in  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  or  $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ ) gives a value which is however two orders of magnitude smaller than the usual dipole-dipole interaction.

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To explain the rich magnetic behaviour of cuprates it is important to analyse not only the dominant isotropic superexchange interaction but also the smaller anisotropic terms due to the spin-orbit coupling [1]. In the case of a  $180^\circ$  Cu-O-Cu bond, this explains for instance the “easy plane” magnetism observed in the standard  $\text{CuO}_2$  plane of orthorhombic [2] or tetragonal [3] cuprates. However, there is another important structural element in many cuprates, namely a rectangular Cu-O-Cu bond. It is present in such cuprates having a  $\text{Cu}_3\text{O}_4$  plane (as in  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  [4] or in  $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  [5]), having  $\text{CuO}_2$  chains ( $\text{Li}_2\text{CuO}_2$  [6,7],  $\text{CuGeO}_3$  [8]) or in ladder compounds [9]. We are going to calculate here the parameters of the anisotropic superexchange interaction for the ideal  $90^\circ$  bond. To incorporate lattice effects we investigate a  $\text{Cu}_2\text{O}_6$  cluster (Fig. 1) - the common structural fragment of the cuprates mentioned. We choose as a representative example the  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  compound for which all important underlying parameters are derived from the extended multi-orbital tight-binding (TB) analysis of its bandstructure. Some results of the TB analysis were presented in a previous publication [10].

In the  $\text{Cu}_3\text{O}_4$  plane of  $\text{A}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  ( $\text{A}=\text{Ba},\text{Sr}$ ) one has to distinguish  $\text{Cu}_A$  with a local orthorhombic symmetry and  $\text{Cu}_B$  with local tetragonal symmetry. Lower than tetragonal local symmetry is obvious at the copper sites in the chains of  $\text{Li}_2\text{CuO}_2$ . This produces an additional feature - a weak higher order pseudodipole part of the magnetic anisotropy in these systems. In the leading orders of the perturbation theory the derived form of the anisotropic superexchange is similar for  $\text{A}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  and  $\text{Li}_2\text{CuO}_2$ . For  $\text{CuGeO}_3$  the analysis should be completed by taking into account the influence of Ge side-groups [8].

The magnetic anisotropy can be calculated in perturbation theory. In second order of the spin-orbit coupling  $\lambda(\vec{L}_A\vec{S}_A + \vec{L}_B\vec{S}_B)$  with a characteristic parameter  $\lambda = 0.1\text{eV}$  for cuprates we obtain (see [11]):

$$\hat{H}_{AB}^{\text{aniso}} = \sum_{\mu\nu} \left[ \Gamma^{\mu\nu} + \Gamma^{\nu\mu} - \delta_{\mu\nu} \left( \sum_{\xi} \Gamma^{\xi\xi} \right) \right] S_A^\mu S_B^\nu, \quad (1)$$

with

$$\Gamma^{\mu\nu} = \left( \frac{\lambda}{2} \right)^2 \sum_{mn} \left\{ \frac{J(m_A, 0_B; n_A, 0_B)}{(E_m^A - E_0^A)(E_n^A - E_0^A)} + (A \leftrightarrow B) \right\} L_{0m}^\mu L_{n0}^\nu, \quad (2)$$

where  $J(m_A, 0_B; n_A, 0_B)$  is the integral of superexchange interaction between the groundstate of  $\text{Cu}_B$  and the excited states  $m_A$  and  $n_A$  of  $\text{Cu}_A$ . The non-zero matrix elements of the orbital momentum are  $L_{0x}^x = L_{0y}^y = i$ ,  $L_{0z}^z = -2i$  with the corresponding Hermitean conjugate ones. We will denote the  $3d$  orbitals of Cu as follows:  $|0\rangle = |x^2 - y^2\rangle$ ,  $|1\rangle = |3z^2 - r^2\rangle$ ,  $|z\rangle = |xy\rangle$ ,  $|x\rangle = |yz\rangle$  and  $|y\rangle = |xz\rangle$  (in the x-y coordinate system of Fig. 1). The small difference between the  $\text{Cu}_A$  and  $\text{Cu}_B$  crystal field splitting, which is inherent to the  $\text{Cu}_3\text{O}_4$  plane, has no meaning for the present purposes and we assume with high accuracy  $\Delta_n = E_n^A - E_0^A \simeq E_n^B - E_0^B$  and  $E_0^A \simeq E_0^B = E_0$ . The values of  $\Delta_n$  derived from the bandstructure data [10] of  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  are listed in Table 1 and these estimates are also relevant for other cuprates.

To analyse (1,2) one has to calculate the different exchange integrals treating the Cu-O hopping ( $\sim t_{pd}$ ) and the O-O hopping ( $\sim t_{pp}, t_{\pi\pi}, t_{p\pi}, t_{pz}$ ) as perturbations. This is justified by the small ratios of these transfer integrals to the characteristic charge transfer energies ( $E_{p,\pi,pz} - E_0$ ). Together with the crystal field splitting the on-site interactions (involving direct and exchange Coulomb terms) at copper and oxygen ions are incorporated into the zero-order Hamiltonian. To evaluate the copper on-site Coulomb interactions the Racah parameters are taken as in Table 1. For B and C parameters the unscreened atomic values are used as explained elsewhere [12]. The parameter A is adopted in such a way that the Coulomb correlation  $U_{00}^d = A + 4B + 3C$  for the groundstate Cu-orbital coincides with the standard value (10.5 eV) given in Ref. [13]. Then one obtains also the other direct ( $U_{01}^d = A - 4B + C$ ,  $U_{0x,y}^d = A - 2B + C$ ) and exchange ( $J_{01}^d = 4B + C$ ,  $J_{0x,y}^d = 3B + C$ ) Coulomb integrals. For the correlation parameter  $U_p$  at oxygen we take the standard value from Ref. [13] and  $J_p$  from [8], which defines also  $U_{p\pi} = U_p - 2J_p$ . The values of the transfer integrals are derived from the tight-binding analysis of the bandstructure [10]. Finally, for proper estimates of the superexchange integrals one needs also the “bare” values for the charge transfer energies  $E_{p,\pi,pz} - E_0$ , instead of screened ones inferred from the bandstructure calculations. To solve

this problem we have used a cluster procedure [14] connecting self-consistently the mean-field (screened) values with “bare” ones for the on-site orbital energies.

To perform calculations in a more effective way we introduce instead of the original in-plane oxygen  $|p_{1,2}\rangle$ - and  $|\pi_{1,2}\rangle$ -orbitals their combinations, like

$$\left\{ \begin{array}{l} |p\rangle \\ |\tilde{p}\rangle \end{array} \right\} = \frac{1}{\sqrt{2}} [|p_2\rangle \mp |p_1\rangle] , \quad \left\{ \begin{array}{l} |\pi\rangle \\ |\tilde{\pi}\rangle \end{array} \right\} = \frac{1}{\sqrt{2}} [|\pi_2\rangle \mp |\pi_1\rangle] , \quad (3)$$

with energies  $\Delta_{p/\tilde{p}} = E_p - E_0 \mp t_{pp}$  and  $\Delta_{\pi/\tilde{\pi}} = E_\pi - E_0 \mp t_{\pi\pi}$ , respectively (Table 1). For brevity we present below only the most important hybridization interaction giving rise to the lowest order contributions (4th order in  $t_{pd}$ ) to the superexchange

$$H_t^{(pd)} = t_{pd} \left[ \sqrt{2}(d_{0A}^\dagger p + d_{0B}^\dagger \pi) + \sqrt{\frac{2}{3}}(d_{1A}^\dagger \tilde{p} - d_{1B}^\dagger \tilde{\pi}) + \sqrt{\frac{2}{3}}(d_{zA}^\dagger \tilde{\pi} - d_{zB}^\dagger \tilde{p}) \right. \\ \left. + \sqrt{\frac{1}{3}}(d_{xA}^\dagger - d_{yB}^\dagger)p_{2z} + \sqrt{\frac{1}{3}}(d_{yA}^\dagger + d_{xB}^\dagger)p_{1z} \right] + h.c. \quad (4)$$

Contributions to the superexchange due to the oxygen orbitals at the right and the left cluster edges are mediated by O-O hybridization, which are taken into account below as the 5-th and 6-th order corrections.

After these preliminaries we are able to estimate the different integrals  $J(m, 0; n, 0)$  entering into (2). Let us start, however, with the discussion of the basic isotropic superexchange between  $\text{Cu}_A$  and  $\text{Cu}_B$  in the groundstate. In our notation that is given by  $J(0_A, 0_B; 0_A, 0_B) \equiv J_{AB}$ . This exchange of 4th order in  $t_{pd}$  and with a dominant ferromagnetic contribution due to the Hund’s rule coupling  $J_p$  at oxygen was estimated already several times (see [8–10,14]). In the next order (6th) of perturbation theory we find an antiferromagnetic contribution which arises due to the hopping  $t_{p\pi}$  [10]. With the parameters chosen that sums up to a resulting ferromagnetic exchange of  $J_{AB} = -6$  meV.

Let us estimate now the other non-zero integrals responsible for the anisotropy (1,2). That has to be considered as additional terms on top of the dominant isotropic ferromagnetic term discussed above. First, we calculate  $J(z_A, 0_B; z_A, 0_B) = J_{A,zz}^{(d)} + J_{A,zz}^{(p)}$  with two contributions in accordance with two possible intermediate virtual states in the 4th order processes. These processes with the corresponding amplitudes and interaction parameters are shown schematically in Fig. 2. For the first contribution  $\sim J_{A,zz}^{(p)}$ , the singlet-triplet splitting in the virtual two-hole state, with occupied oxygen  $|\pi\rangle$ - and  $|\tilde{\pi}\rangle$ -orbitals, is due to the correlation interaction  $U_p$ . Then taking into account the other oxygen orbitals at the cluster edges, which gives the 5th order correction  $\sim t_{pp}$ , we obtain the result

$$J_{A,zz}^{(p)} = -\frac{4}{3}t_{pd}^4 \left( \frac{1}{\Delta_\pi} + \frac{1}{\Delta_{\tilde{\pi}}} \right)^2 \left( \frac{1}{\Delta_{\pi\tilde{\pi}}^T} - \frac{1}{\Delta_{\pi\tilde{\pi}}^S} \right) \left( 1 + 2t_{pp} \left( \frac{1}{\Delta_p} - \frac{1}{\Delta_{\tilde{p}}} \right) \right) , \quad (5)$$

with the triplet and singlet energies  $\Delta_{\pi\tilde{\pi}}^T = \Delta_\pi + \Delta_{\tilde{\pi}}$ ,  $\Delta_{\pi\tilde{\pi}}^S = \Delta_\pi + \Delta_{\tilde{\pi}} + U_p$ , respectively. The 5th order correction gives only a 10 per cent decrease. In the intermediate state of the second contribution  $J_{A,zz}^{(d)}$ , the two holes meet at the same  $\text{Cu}_B$  ion, but in different orbitals  $|0_B\rangle$  and  $|1_B\rangle$ . They interact due to the Hund’s coupling  $\sim J_{01}^d$  to give

$$J_{A,zz}^{(d)} = -\frac{4}{9} \frac{t_{pd}^4}{\Delta_\pi^2} \left[ \frac{1}{U_{01}^d - J_{01}^d} - \frac{1}{U_{01}^d + J_{01}^d} \right] \simeq -\frac{4}{9} \frac{t_{pd}^4}{\Delta_\pi^2} \frac{2J_{01}^d}{(U_{01}^d)^2} , \quad (6)$$

without any correction of fifth order. The integral  $J(z_B, 0_A; z_B, 0_A)$  can be obtained by replacing  $\pi, \tilde{\pi} \leftrightarrow p, \tilde{p}$ . Analogously we find  $J(x_A, 0_B; x_A, 0_B) = J_{A,xx}^{(d)} + J_{A,xx}^{(p)}$  with

$$J_{A,xx}^{(p)} \simeq -\frac{t_{pd}^4}{3} \left( \frac{1}{\Delta_{p_z}} + \frac{1}{\varepsilon_\pi} \right)^2 \frac{2J_p}{(\Delta_{p_z} + \varepsilon_\pi + U_{p\pi})^2} \left( 1 + \frac{2t_{\pi\pi}}{\Delta_{p_z}} \right) , \quad (7)$$

$$J_{A,xx}^{(d)} \simeq -\frac{1}{9} \frac{t_{pd}^4}{\Delta_{p_z}^2} \frac{2J_{0y}^d}{(U_{0y}^d)^2}, \quad (8)$$

where  $\Delta_{p_z} = E_{p_z} - E_0$  is the on-site energy of the out-of-plane  $|p_z\rangle$ -orbital and  $\varepsilon_\pi = \Delta_\pi + t_{\pi\pi}$ . The same result also holds for  $J(x_B, 0_A; x_B, 0_A)$  and for  $J(y_A, 0_B; y_A, 0_B) = J(y_B, 0_A; y_B, 0_A)$  since  $U_{0x}^d = U_{0y}^d$  and  $J_{0x}^d = J_{0y}^d$ .

The pseudodipolar part of the superexchange for the Cu-O-Cu bond in a lattice arises due to deviations from the local tetragonal symmetry. Taking as a representative example the  $\text{Cu}_3\text{O}_4$  plane this deviation occurs at the  $\text{Cu}_A$  sites. The orthorhombic energy splitting between the  $|x'\rangle$ - and  $|y'\rangle$ -orbitals (see the  $x'$ - $y'$  coordinate system of Fig. 1) is derived from the bandstructure results at the  $\Gamma$  point to be  $\delta\varepsilon_{xy} \approx 30$  meV. That corresponds to a mixed matrix element  $\langle x|H|y\rangle = \delta\varepsilon_{xy}/2$  in the  $x$ - $y$  coordinate system chosen in the calculation. The second source for the pseudodipolar interaction is the difference in the transfer integrals  $\delta t_{p_z} = t_{p_z}^\perp - t_{p_z}^\parallel$ , between  $|p_z\rangle$ -orbitals perpendicular or parallel to the A-B bond line. A rough estimate derived from the bandstructure results [10] is found to be  $\delta t_{p_z} \approx 40$  meV. Using these deviations from tetragonality as an additional perturbation we obtain the following estimate for the only non-zero off-diagonal exchange integrals

$$J(x_A, 0_B; y_A, 0_B) = J(y_A, 0_B; x_A, 0_B) \sim \xi J^{(4)}(x_A, 0_B; x_A, 0_B) \quad (9)$$

starting from the 4th order term of the diagonal exchange ((7) and (8) without 5th order correction). The reduction factor is

$$\xi = \frac{\delta\varepsilon_{xy}}{\Delta_x} + 2 \frac{\delta t_{p_z}}{\Delta_{p_z}}. \quad (10)$$

Using the parameters for  $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  (see Table 1) we obtain finally from (2)-(10) the following numbers for the anisotropic superexchange

$$\Gamma^{zz} = -0.65\text{meV}, \quad \Gamma^{xx} = \Gamma^{yy} = -10\mu\text{eV}, \quad |\Gamma^{xy}| \sim 0.2\mu\text{eV}. \quad (11)$$

In terms of the spin components parallel and perpendicular to the bond, the Hamiltonian (1) takes the following form

$$\hat{H}_{AB}^{\text{aniso}} = J_\parallel S_A^\parallel S_B^\parallel + J_\perp S_A^\perp S_B^\perp + J_z S_A^z S_B^z, \quad (12)$$

with  $J_\parallel = -\Gamma^{zz} + 2\Gamma^{xy}$ ,  $J_\perp = -\Gamma^{zz} - 2\Gamma^{xy}$  and  $J_z = \Gamma^{zz} - 2\Gamma^{xx}$ . It should be noted that in spite of the nontetragonality of the particular bond under consideration we did not find in the leading orders of the perturbation procedure any process which could lead to the Dzyaloshinskii-Moryia [11] spin coupling.

Let us discuss now the consequences for several cuprates and start with the  $\text{Cu}_3\text{O}_4$  plane. First, one has to compare the derived value of the pseudodipolar part of the anisotropic superexchange  $J_{pd}^{se} = (J_\parallel - J_\perp)/2 = 2\Gamma_{xy}$  with the estimate [5]  $J_{dd} \approx 20 \mu\text{eV}$  for the usual dipole-dipole interaction for the  $\text{Cu}_A\text{-Cu}_B$  bond. The small value of  $J_{pd}^{se}$  supports the suggestion [5] that the weak ferromagnetic moment observable in  $\text{A}_2\text{Cu}_3\text{O}_4\text{Cl}_2$  is mainly due to the usual dipole-dipole interaction. Effects of the other kind of anisotropy given by  $\Delta J = (J_\parallel + J_\perp)/2 - J_z = -2(\Gamma_{zz} - \Gamma_{xx}) > 0$  could be revealed only in a more general context. Actually, to predict the low-temperature magnetic structure in the above compound one has to take into account the main interactions (including the isotropic and anisotropic terms) for  $\text{Cu}_A\text{-Cu}_A$  and  $\text{Cu}_B\text{-Cu}_B$  bonds in the  $\text{Cu}_3\text{O}_4$  plane. This requires a more extended analysis for these two interacting antiferromagnetic subsystems [1,5].

At the same time, in  $\text{Li}_2\text{CuO}_2$ , the estimate  $\Delta J > 0$  is important to explain the magnetic ordering. Based on preliminary bandstructure results [15] one may infer that the relevant parameters for  $\text{Li}_2\text{CuO}_2$  will be only slightly changed in comparison to Table 1. Therefore, it can be expected that the above result for  $\Delta J$  remains qualitatively correct. At low temperatures, for a chain with ferromagnetically aligned spins, the anisotropy  $\Delta J > 0$  prefers a spin direction parallel to the  $z$  axis, i.e. perpendicular to the chain plaquettes. That agrees with the experimental situation [6,7]. The measured energy gap in the spin wave

spectrum [7] leads to a uniaxial anisotropy which is in agreement with our estimate for  $\Delta J$ . But the values of the isotropic superexchange coupling reported in [7] are about one order of magnitude smaller than that estimated from the bandstructure calculation [16] and characteristic also for other cuprates. It would be interesting to reanalyse the spin wave spectrum starting from a spin Hamiltonian based on the microscopic electronic structure. Some additional complications should be noted as well. Actually, a magnetic frustration occurs in  $\text{Li}_2\text{CuO}_2$  since the isotropic antiferromagnetic superexchange for second neighbours within a chain is rather strong. That is expected [15,16] to exceed even the ferromagnetic coupling for nearest neighbour spins. The stability of the overall magnetic structure in  $\text{Li}_2\text{CuO}_2$  with antialigned ferromagnetic chains can be explained due to a considerable three dimensional spin coupling in this compound [15,16].

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## TABLES

TABLE 1: Parameters (in eV) to calculate the magnetic anisotropy.

copper crystal field splitting			transfer integrals			oxygen correlations		
$\Delta_1$	$\Delta_z$	$\Delta_{x,y}$	$t_{pd}$	$t_{pp}$	$t_{\pi\pi}$	$U_p$	$U_{p\pi}$	$J_p$
0.65	1.08	1.32	1.40	0.80	0.45	4.0	3.2	0.4

oxygen on-site energies					copper correlations		
$\Delta_\pi$	$\Delta_p$	$\Delta_{pz}$	$\Delta_{\bar{\pi}}$	$\Delta_{\bar{p}}$	$A$	$B$	$C$
3.5	3.9	4.0	4.4	5.5	8.16	0.15	0.58

## FIGURES

FIG. 1: The  $\text{Cu}_2\text{O}_6$  cluster used to calculate the magnetic anisotropy (full circles: copper, open circles: oxygen) with the ground state orbitals  $|0\rangle$  at copper and the in-plane oxygen orbitals (full lines:  $|p\rangle$ -orbitals and broken lines  $|\pi\rangle$ -orbitals). Also shown are the two coordinate systems mentioned in the text.

FIG. 2: Examples for 4th order processes which contribute to  $J_{A,zz}^{(d)}$  and  $J_{A,zz}^{(p)}$ .



